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(54) Method of oxidatively degrading an olefinic polymer to produce an oxidised polymer product useful as a viscosity index improvement agent for a lubricating oil.

(57) A method of oxidatively degrading an olefinic polymer comprises oxidising the olefinic polymer in an inert solvent in the absence of molecular oxygen and in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised polymer product is obtained. The oxidised polymers produced by this method can be further reacted with a nitrogen-containing compound such as a polyalkylene polyamine. The oxidised polymer products are of value as viscosity index improvement agents when incorporated in lubricating oil compositions.

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1      Method of oxidatively degrading an olefinic polymer  
      to produce an oxidised polymer product useful as a  
viscosity index improvement agent for a lubricating oil

5      This invention relates to a method of oxidatively  
degrading an olefinic polymer and to the use of the  
oxidised polymer so-produced as a viscosity index  
improvement agent in a lubricating oil composition.

An important property of a lubricant composition  
10     is the rate at which its viscosity changes as a function  
of temperature. The relationship between the viscosity  
and temperature is commonly expressed in terms of the  
viscosity index (V.I.). Lubricant compositions which  
change little in viscosity with variations in temperature  
15     have greater viscosity index than do compositions whose  
viscosity is materially affected by changes in tempera-  
ture. It is readily apparent, therefore, that one of the  
major requirements of lubricating oils or other hydro-  
carbon oil products is their satisfactory viscosity-tem-  
perature characteristics. These characteristics are  
20     necessary in order that the viscosity of the oil will not  
become too low but will show an equally good performance  
within a relatively wide temperature range to which it  
may be exposed in service. The wider the possible  
25     temperature variations, the smaller should be the change  
in viscosity with temperature. Hence, the viscosity-  
temperature characteristics of a lubricant which is used  
in applications where wide variations in temperature are  
encountered are of great importance and lubricant  
30     compositions having high viscosity indices are highly  
desirable.

A variety of polymeric or high molecular weight  
materials have been described as viscosity index  
improvers for lubricants and have been prepared via an  
35     air or oxygen sparging oxidation process which involves  
the use of molecular oxygen in at least one step in the  
preparation thereof. For example: U.S. Patent No.

- 1    3,417,020 teaches lubricating oil compositions of  
improved viscosities containing degraded  
ethylene-alpha-olefin polymers wherein the degraded  
polymers have been hydroxylated. The hydroxylated  
5    degraded polymers are prepared by hydroperoxidizing the  
polymer with subsequent reduction of the hydroperoxide  
groups to yield degraded products containing hydroxyl  
groups and minor amounts of carboxyl, keto and aldehyde  
groups.
- 10      U.S. Patent No. 3,756,954 teaches the preparation  
of viscosity index improvers prepared by air oxidation of  
interpolymers of ethylene and propylene in the presence  
of an aliphatic amine.
- 15      British Patent Application No. 2,040,296A teaches  
the preparation of a viscosity index improver additive by  
oxidatively and mechanically degrading an ethylene  
copolymer containing as one of its components from 0.05  
to 3% of 2,5-norbornadiene.
- 20      U.S. Patent No. 3,316,177 teaches reaction of  
polyamine with the reaction product of maleic anhydride  
with an oxidized interpolymer of ethylene and propylene,  
as a sludge dispersant in lubricant and fuel  
compositions.
- 25      U.S. Patent No. 3,404,091 describes the prepara-  
tion of nitrogen containing polymers, useful as sludge  
dispersants and viscosity index improvers, by grafting  
polar monomers such as acrylonitrile on to hydroperoxi-  
dized ethylene-propylene copolymers.
- 30      U.S. Patent No. 3,687,849 describes the prepara-  
tion of viscosity index improvers, pour point depressants  
and dispersants, for fuels and lubricants, by grafting  
various unsaturated monomers on to a degraded, oxidized,  
interpolymer of ethylene and propylene.
- 35      U.S. Patent No. 3,687,905 describes the prepara-  
tion of additives for fuels and lubricants by the  
reaction of an unsaturated acid, such as maleic acid or  
anhydride, with an oxidized, degraded interpolymer of  
ethylene and propylene, followed by reaction with a

1 polyamine.

U.S. Patent No. 3,769,216 discloses the preparation of lube oil additives by the condensation of an amine with an oxidized ethylene-propylene copolymer, 5 prepared by air blowing in the presence of a peroxide (also see U.S. Patent 3,785,980), or by mastication of the polymer in the presence of oxygen.

While not related to the preparation of viscosity index improvers, other oxygen-sparging oxidation methods 10 applied to olefinic polymers are described in the prior art, for example, in U.S. Patent Nos. 3,153,025, 3,110,708 and 3,232,917.

With respect to these prior art methods, there is considerable concern about the safety aspects such as the 15 possibility of an explosion using air oxidation of an olefinic polymer solution involving relatively large quantities of molecular oxygen and a large volume of hydrocarbon.

It has now been found in accordance with the 20 invention that the oxidation of olefinic polymers is advantageously carried out in solution using a mixture of organic peroxide and hydroperoxide as the oxidizing agent. This system is preferred because it forms a single-reaction phase with the polymer solution, it is 25 relatively non-corrosive, and it does not have the hazards associated with the air oxidation of hydrocarbons.

Thus in accordance with one aspect of the invention, there is provided a method of oxidatively 30 degrading an olefinic polymer in the absence of molecular oxygen, which comprises oxidizing the olefinic polymer in an inert solvent in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount 35 sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised

1 polymer product is obtained.

The oxidized polymer obtained by the foregoing method may be further reacted with one or more functional group-containing compounds, such as non-tertiary 5 nitrogen-containing compounds. Both the oxidized polymer and the functionalized derivatives thereof are viscosity-index improvement agents for lubricating oils. The polymers so produced also show excellent dispersancy properties in lubricating oils and have excellent 10 thickening power and shear stability.

The term "olefinic polymer" is used herein to mean polymers derived from olefinically unsaturated hydrocarbon monomers. The polymer may be a homopolymer, 15 a copolymer, which term includes random, and block copolymers, or a terpolymer or tetrapolymer, etc.

Suitable homopolymers include polybutenes, such as polyisobutene having an  $\bar{M}_n$  in the range 5,000 to 60,000, preferably in the range 10,000 to 45,000. Suitable 20 copolymers include ethylene copolymers, especially copolymers of ethylene and a C<sub>3</sub>-C<sub>8</sub> alpha-olefin such as ethylene/propylene, e.g. ethylene/propylene copolymers containing from 20 to 65, preferably from 35 to 45 mole percent propylene and having an  $\bar{M}_n$  in the range 10,000 to 200,000, preferably from 20,000 to 70,000, and copolymers 25 of a vinyl aromatic monomer, e.g. styrene, alphamethyl styrene or vinyl naphthalene, and a conjugated diene monomer, e.g. butadiene or isoprene, of which hydrogenated block copolymers containing from 10 to 40, preferably from 15 to 35 weight percent of the vinyl 30 aromatic monomer and having an  $\bar{M}_n$  in the range 25,000 to 125,000, preferably from 50,000 to 125,000, are preferred. Such polymers are described in, for example, U.S. Patents Nos. 3,994,815; 3,775,329; 3,668,125 and 3,763,044. Suitable random copolymers are described in 35 for example, U.S. Patents Nos. 3,554,911; 3,630,905; 3,752,767 and 3,772,169. Suitable terpolymers include terpolymers of ethylene, a C<sub>3</sub> to C<sub>8</sub> straight- or branched-

1 chain alpha-olefin, e.g. propylene, and a non-conjugated  
acyclic or alicyclic diolefin, e.g. 1,4-hexadiene,  
1,5-heptadiene, 1,6-octadiene, 1,4-cyclohexadiene, 5-  
methylene-2-norbornene or 5-ethylidene-2-norbornene,  
5 generally containing from 30 to 85, preferably from 40 to  
70 mole percent ethylene, from 15 to 70, preferably from  
30 to 60 mole percent alpha-olefin and from 0.5 to 20  
mole percent, preferably from 1 to 15, even more  
preferably from 2 to 10 mole percent diene and having an  
10  $M_n$  in the range from 15,000 to 200,000, preferably from  
20,000 to about 70,000. Preferred terpolymers are  
terpolymers of ethylene, propylene and 1,4-hexadiene or  
5-ethylidene-2-norbornene. Suitable tetrapolymers  
include tetrapolymers of ethylene, a C<sub>3</sub> to C<sub>8</sub> straight-  
15 or branched-chain alpha-olefin and two non-conjugated  
acyclic or alicyclic diolefins. The preparation of the  
terpolymers, using Ziegler-Natta catalysts, is described,  
for example, in U.S. Patents Nos. 2,933,489, 3,000,866  
and 3,093,621. These terpolymers and tetrapolymers,  
20 which are primarily produced for use in elastomeric  
compositions, are characterized by the absence of chain  
or backbone unsaturation and contain sites of unsatura-  
tion in groups which are pendant to or in cyclic  
structures outside of the main polymer chain. It is an  
25 advantage of the present invention that oxidation occurs  
substantially on the main backbone chains of the polymers  
in preference to the groups pendant to or outside the  
backbone chain.

Mixtures of polymers may also be used, if so  
30 desired, in the process of the invention. Thus blends  
may be formulated to provide desirable properties, e.g.  
improved low temperature thickening. Suitable mixtures  
of polymers include mixtures of two or more ethylene/  
propylene copolymers having different ethylene-propylene  
35 ratios and/or molecular weights and mixtures of an  
ethylene/propylene copolymer and a polyisobutene.

In accordance with the present invention, the

1 aforementioned olefinic polymers are employed as starting  
materials in a controlled oxidation reaction using a  
mixture of at least one peroxide and at least one  
hydroperoxide referred to hereinabove as the oxidant  
5 mixture. More specifically, the oxidized olefinic  
polymers resulting from this invention are prepared by  
dissolving the olefinic polymer in an inert solvent at a  
temperature generally in the range of from 60°C to 250°C,  
using agitation. A mixture of radical initiators is  
10 added to the reaction medium under a pressure of from 0  
to 1,000 psig (1 to 70.3 kg/sq.cm) and the reaction is  
continued for a period of from about 0.05 to 20 hours.  
There is essentially no introduction of oxygen from a  
separate source into the reaction medium during the  
15 oxidation reaction.

The final polymeric product may be recovered from  
solution by evaporation of the solvent or by precipita-  
tion with a non-solvent or by any other suitable method.  
Alternatively, prior to removal of the inert solvent, a  
20 lubricating oil may be added directly to the reaction  
mixture and the inert solvent removed by vacuum  
distillation.

The oxidized olefinic polymer can be made in batch  
or continuous operation. In batch operation, the  
25 individual components are added to a suitable reaction  
vessel together or in discrete portions and dissolved in  
an inert solvent. In continuous operation the reactant  
or reactants are added continuously to a horizontal or  
vertical reaction zone at appropriate feed rates in a  
30 diluent or neat at temperatures to promote easy handling,  
reaction and solubility.

The compositions of this invention have a thickening  
power in the range of from 10-35 cSt. "Thickening  
power" as used herein is defined as the viscosity at  
35 100°C of a neutral oil having a viscosity at 40°C of 28.6  
cSt and at 100°C of 4.7 cSt, containing 2.8 weight  
percent of the dry polymeric composition. Thickening  
power is thus measured as an actual viscosity of the oil

1 due to incorporation of the polymer. Thickening power is  
directly related to the molecular weight of the polymer,  
but is used instead of molecular weight because of the  
ease of measurement and greater practical significance of  
5 data. While the thickening power of the compositions of  
this invention may be broadly defined as being in the  
range of 10-35 cSt, thickening power is more usually in  
the range of 15-25 cSt.

The oxidation is carried out in the presence of a  
10 mixture of at least one peroxide and at least one  
hydroperoxide in a mole ratio of peroxide to hydroper-  
oxide in the range from 3.2:1 to 0.4:1 and preferably in  
the range from 1.7:1 to 0.8:1. Surprisingly, it has been  
found that use of the combination is much more efficient  
15 in oxidizing and degrading the olefinic polymer than the  
use of either the peroxide or hydroperoxide alone.

Representative of the peroxides which may be used  
in the mixture are, for example, cumene peroxide, dicumyl  
peroxide, benzoyl peroxide, dilauryl peroxide, di(n-  
20 propyl)peroxydicarbonate, tertiary butylperoxyisobuty-  
rate, 2,5-dimethyl-2,5-di(t-butylperoxy) hexane and  
acetyl cyclohexylsulfonyl peroxide. Representative of  
the hydroperoxides which may be used are, for example,  
cumene hydroperoxide, hydrogen peroxide, tertiary butyl  
25 hydroperoxide and 2,5-dihydroperoxy-2,5-dimethylhexane.  
It is also possible to use a single compound which  
contains at least one peroxide group and at least one  
hydroperoxy group, or a mixture of such compounds. The  
concentration of the oxidant mixture relative to the  
30 olefinic polymer in solution is generally in the range  
from 1 to 20% by weight, preferably from 2 to 15 percent  
and most preferably from 5 to 12% by weight.

The oxidation is carried out in a solvent  
substantially inert to the reaction conditions. Solvents  
35 such as toluene, xylene, hexane, or mineral neutral oils  
can be used. Preferred solvents are benzene, chloroben-  
zene and t-butylbenzene. The solvent may suitably be  
present in an amount in the range from 20 to 99%.

1 preferably from 50 to 95%, and more preferably from 70 to  
90% by weight, based on the weight of the olefinic  
polymer.

The oxidised polymer product obtained by the  
5 oxidation reaction is an oil-soluble product of lower  
molecular weight than the starting material. The  
molecular weight depends upon the extent and conditions  
employed during the oxidation reaction. Ultimately, the  
intermediate oxidized polymers are converted by oxidation  
10 reactions to fragmented or degraded polymer materials  
containing carbonyl groups. The more vigorous the  
oxidation conditions and the longer the length of time  
maintaining such conditions, the greater the number of  
carbonyl groups introduced into the starting material.  
15 It is sufficient, however, than on an average at least  
one carbonyl, preferably in the form of a carboxyl-  
carbonyl, is introduced into each molecule of the  
starting material.

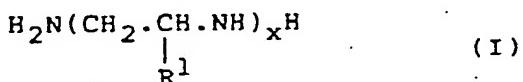
The oxidized polymer materials have a viscosity  
20 average molecular weight of from about one-half to  
one-tenth of the molecular weight of the original  
material. The product of the oxidation process will  
generally have from 0.01% to 1% by weight oxygen and  
preferably from 0.2% to 0.8% by weight oxygen.

In accordance with another aspect of the invention  
25 there is provided a lubricating oil composition  
comprising an oil of lubricating viscosity and, as a  
viscosity index improvement agent, an oxidized olefinic  
polymer product containing carbonyl groups obtained by  
30 the method of the invention as hereinbefore described.  
Preferably the polymer product is present in the  
lubricating oil in an amount of from 0.05 to 20% by  
weight.

It is believed that the majority of the carbonyl  
35 groups introduced into the polymer, or at least the  
ethylene/propylene copolymers, by the oxidative method of  
the present invention tend to be carboxylic acid carbonyl  
groups rather than aldehydrocarbonyl and ketocarbonyl

1 groups. Carboxylic acid carbonyl and ketocarbonyl groups  
are favoured for the further chemical conversion of the  
oxidized polymer. The oxidized olefinic polymers may be  
reacted through their carbonyl groups with a variety of  
5 other reagents, e.g., hydrogen or nitrogen, oxygen,  
sulfur, boron and/or phosphorus-containing compounds to  
form multifunctional products. It is preferred to react  
the oxidized olefinic polymers with one or more nitrogen-  
containing compounds (other than a tertiary nitrogen  
10 compound), such as ammonia and organic amines which may  
be mono, di or polyamines containing at least one primary  
or secondary amino group, and, advantageously  
polyalkylene polyamines having the general formula:

15



wherein each R<sup>1</sup> is hydrogen or a C<sub>1</sub> to C<sub>6</sub> alkyl group,  
20 preferably hydrogen, and x is an integer in the range  
from 1 to 10, preferably in the range from 2 to 5, to  
form a nitrogen-containing product having both viscosity  
index improvement and dispersancy properties. Examples  
of suitable nitrogen-containing compounds include 1,2-  
25 diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane;  
1,6-diaminohexane; diethylene triamine, triethylene  
tetramine, tetraethylene pentamine; 1,2-propylene  
diamine; di-(1,2-propylene) triamine, di-(1,3-propylene)  
triamine and N,N-di-(2-aminoethyl) ethylene diamine.

30 Other polyamine compounds that may be used include  
the N-aminoalkyl piperazines of the general formula:

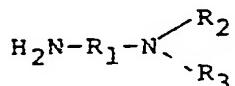
$$\text{NH}_2 - (\text{CH}_2)_n - \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 - \text{CH}_2 \end{array} - \text{N} - \text{R}$$

wherein n is from 1 to 3, and R is hydrogen or an

- 1 aminoalkyl radical containing from 1 to 3 carbon atoms. Specific examples include N-(2-aminoethyl) piperazine, N-(2-aminoisopropyl) piperazine and N,N'-di-(2-aminoethyl) piperazine.
- 5 The polyalkylene polyamines which may be used in the practice of this invention can be either pure alkylene amines or they can be commercial mixtures. For example, one process for preparing alkylene amines involves the reaction of an alkylene chloride such as
- 10 ethylene chloride or propylene chloride with ammonia, which results in the production of somewhat complex mixtures of alkylene amines including various piperazines. One useful commercial product is a mixture of ethylene amines prepared by the reaction of ethylene
- 15 chloride and ammonia and having a composition that corresponds to that of a tetraethylene pentamine. One such mixture is known in the trade under the name "Polyamine H".

Still other alkylene amino compounds that can be used include dialkylamino alkyl amines such as dimethylamino methyl amine, dimethylamino propyl amine, and methylpropylamino amyl amine. These may be characterized by the general formula:

25



wherein R<sub>1</sub> is an alkylene radical, e.g., an ethylene, propylene, or butylene radical, and R<sub>2</sub> and R<sub>3</sub> are C<sub>1</sub> to C<sub>5</sub> alkyl radicals.

Other useful amines include N,N-di-(2-hydroxyethyl)-1,3-propylene diamine; 3-dodecyloxypropylamine; N-dodecyl-1,3-propane diamine; tris-hydroxymethyl aminomethane, diisopropanolamine and diethanolamine. There may also be used the mono-succinimide, formed by reacting an alkenyl-succinic anhydride such as

- 1 polyisobutene succinic anhydride with either a diamine or a polyalkylene polyamine having the formula (I).  
The reaction conditions for the reaction of carbonyl groups with nitrogen-containing compounds are well-known in the art. Thus, for example, the condensation of the oxidized rubbery polymers containing a plurality of carbonyl groups and preferably carboxylic acid carbonyl groups with a primary or secondary amine to an aminated carbonyl compound useful as a lubricating oil additive is carried out in the presence of a substantially inert solvent at a temperature generally of from 100°C to 280°C for a period of generally from 1 to 24 hours. Typical solvents include the hydrocarbon oil into which the product is designed to be incorporated.
- 5 Alternatively, another solvent miscible in the lubricating oil and liquid at the reaction temperature may serve as the reaction medium. This would include aromatics such as mixed xylenes, as well as aliphatic oils and halogenated materials such as o-dichlorobenzene.
- 10 The mole ratio of polyamine to oxidized polymer is generally in the range from 0.2 to 2.5 moles of amine per mole of oxidized polymer.

Methods for preparing aminated polyolefins are described for example in U.S. Patents Nos. 3,785,980; 25 4,132,661 and 4,317,772.

In a similar manner other preferred derivatives of the oxidized olefinic polymers which are useful as viscosity-index improvers may be formed by reaction with (1) reducing agents or hydrogen to form hydroxylated polymers are described in U.S. Patent No. 3,388,067, which hydroxylated polymers may be further reacted with isocyanates as described in U.S. Patent No. 3,404,092, (2) oxygen-containing compounds such as maleic anhydride followed by reaction with a polyamine as described in 30 U.S. Patents Nos. 3,687,905 and 3,316,177 and (3) sulfur compounds or sulfur compounds and an amine as described in U.S. Patents Nos. 4,317,738 and 4,320,017.

1 It will be appreciated that the invention includes  
within its scope a lubricating oil composition comprising  
an oil of lubricating viscosity and, as a viscosity index  
improvement agent, a further-reacted and functionalized  
5 oxidized olefinic polymer product as described above.  
Preferably the polymer product is present in the  
lubricating oil in an amount of from 0.05% to 10% by  
weight.

The lubricating oils used in the compositions of  
10 the invention are oils of lubricating viscosity, and  
particularly of the type useful in internal combustion  
engines and can be predominantly paraffinic or  
naphthenic, or they can be a mixture of both types of  
mineral oils, as well as synthetic oils which include  
15 polymers of various olefins, generally of 10 carbon atoms  
or higher, and alkylated aromatic hydrocarbons. In  
general, the lubricating oil will preferably be a  
relatively highly refined mineral oil of predominantly a  
paraffinic nature and will have a viscosity in the range  
20 of from 2 to 20 cSt at 100°C.

Other additives, such as detergents, rust  
inhibitors, anti-oxidants, anti-wear agents, etc., may  
also be present in the lubricating oil composition.  
These other additives will be present in conventional  
25 concentrations. Preferred additives which may be present  
in the lubricating oil composition in effective amounts,  
and preferably in the concentration range of from 0.01%  
to 5%, include neutral and overbased alkali and alkaline  
earth metal sulfonates or phenates or combinations  
30 thereof, a metal dihydrocarbyl dithiophosphate such as a  
zinc dialkyl dithiophosphate and/or an alkenyl succini-  
mide or succinate or mixtures thereof.

The invention is illustrated by the following non-  
limitative Examples.

35

Example 1

A pipe reactor consisting of 7.62 m of 12.7 mm  
carbon steel pipe heated by steam tracing was used for

1 this reaction. A solution containing 8% by weight of an  
ethylene/propylene/1,4-hexadiene terpolymer (a product  
manufactured by Du Pont Company, Wilmington, Delaware,  
USA and sold under the trade name Ortholeum 2038, which  
5 is a terpolymer having about 60 mole percent ethylene  
groups, 39 mole percent propylene groups and 1 mole  
percent 1,4-hexadiene groups and having a molecular  
weight of about 250,000) in chlorobenzene was first  
pumped through a hot oil heat exchanger and heated to a  
10 temperature of 167°C. The solution was then fed into the  
reactor at 340 g/min. The reactor was kept at 155°C  
using steam and the pressure was maintained at 200 psig  
(14 kg/sq.cm). At the front end of the reactor two other  
solutions were pumped in - a 50% by weight dicumyl  
15 peroxide in chlorobenzene at 2 ml/min. and an 8% by  
weight hydrogen peroxide in water at 8 ml/min. At the  
end of the reactor 100 Neutral oil was line mixed with  
the reaction mixture at 272.4 g/min.

20 50 gallons (0.189 m<sup>3</sup>) of the reaction mixture  
containing oil was stripped in a 100 gallon (0.379 m<sup>3</sup>)  
glass kettle at 300°F (148.9°C) and 20 mm Hg for 1 hour.  
Then, it was transferred to a 50 gallon (0.189 m<sup>3</sup>)  
stainless steel kettle and stripped at 400°F (204.4°C)  
and 20 mm Hg for 1 hour.

25 The final product has the following properties:  
Viscosity at 100°C (9.75% polymer product by weight)=  
281.6 cSt  
Viscosity of 2.8% solution in 100 N oil = 17.0 cSt  
(Thickening Power)

30 Example 2

The product of Example 1 was line mixed with a  
3.7% solution of ethylene diamine (EDA) in C<sub>7-9</sub> aromatic  
hydrocarbon solvent mixture. The polymer solution was  
pumped at 133.5 ml/min. and the EDA solution was pumped  
35 at 33.4 ml/min. The total mixture was then fed into a  
wiped film evaporator kept at 450°F (232.2°C). The  
stripped product was filtered through a 100 µ filter and

1 had the following properties:

Flash Point = 390°F (198.9°C)

Viscosity at 100°C (9.75% by weight product) =

426.4 cSt

5 Viscosity of 2.8% solution in 100 N oil = 20.7 cSt

(at 100°C)

Nitrogen content = 149 ppm.

Multi-grade lubricating oils with good dispersancy  
and shear stability were prepared using the product of

10 this Example.

Example 3

A pipe reactor consisting of 7.62 m of 12.7 mm carbon steel pipe heated by steam tracing was used for this reaction. A solution containing 8% by weight of the 15 ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 in chlorobenzene was first pumped through a hot oil heat exchanger and heated to a temperature of 216°C. The solution was then fed into the reactor at 0.8 lb/min. (0.36 kg/min). The reactor was kept at 188°C using steam 20 and the pressure was maintained at 200 psig (14.06 kg/cm<sup>2</sup>). At the front end of the reactor two other solutions were pumped in - a 6.25% by weight dicumyl peroxide in chlorobenzene at 2 ml/min. and a 25% by weight cumene hydroperoxide in chlorobenzene at 9.2 25 ml/min. At the end of the reactor 100 Neutral oil was line mixed with the reaction mixture at 0.36 lbs/min (0.16 kg/min).

30 50 gallons (0.189 m<sup>3</sup>) of the reaction mixture containing oil was stripped in a 100 gallon (0.379 m<sup>3</sup>) glass kettle at 300°F (148.9°C) and 20 mm Hg for 1 hour. Then it was transferred to a 50 gallon (0.189 m<sup>3</sup>) stainless kettle and stripped at 400°F (204.4°C) and 20 mm Hg for 1 hour.

The final product had the following properties:

35 Viscosity at 100°C (15% polymer product by weight) =

2111 cSt

Viscosity of 2.8% solution in 100 N oil = 19.8 cSt

## 1       (Thickening Power).

The above-mentioned product was line mixed with a 3.75% solution of ethylene diamine (EDA) in C<sub>7-9</sub> aromatic hydrocarbon solvent mixture. The polymer solution was 5 pumped at 133.5 ml/min. and the EDA solution was pumped at 33.4 ml/min. The total mixture was then fed into a wiped film evaporator kept at 450°F (232.2°C). The stripped product was filtered through a 100 μ filter and had the following properties:

- 10     Flash Point = 300°F (148.9°C)  
Viscosity at 100°C (15% by weight product) =  
2558 cSt  
Viscosity of 2.8% solution in 100 N oil = 20.5 cSt  
(at 100°C)
- 15     Nitrogen content = 98 ppm.

Multi-grade lubricating oils with good dispersancy and shear stability were prepared using the foregoing product of this Example.

Example 4

20     Eighty grams of the ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 was dissolved in 920 g of chlorobenzene at 110°C with stirring. The solution was cooled to about 25°C after which a mixture of cumene hydroperoxide and dicumyl peroxide, in the mole ratios 25 shown in Table I below, were added thereto with mixing. The reaction mixture was pumped at 19.7 g/min into a 50 ml reactor tube (a one quarter inch (6.35 mm) stainless steel tubular reactor) which was maintained at 180°C and 200 psig (14.06 kg/cm<sup>2</sup>). The residence time in the 30 reactor was 2.75 minutes.

To 500 g of the reacted mixture were added 267 g of 100 Neutral oil. The chlorobenzene was removed from this mixture by distillation at 200°C and 20 mm Hg pressure yielding a 15% by weight solution of the 35 oxidized polymer in oil.

A portion of the final product solution was then diluted to 2.8% by weight polymer using additional 100

1 Neutral oil. The viscosity of the resulting 2.8%  
 solution at 100°C in centistokes is what is defined as  
 Thickening Power (TP).

5 The data in Table I demonstrates the effect of  
 varying the mole ratio of peroxide to hydroperoxide on  
 the thickening power of the oxidized polymer.

TABLE I

10	Run No.	Moles		Mole Ratio of	
		Dicumyl Peroxide	Cumene Hydroperoxide	Peroxide to Hydroperoxide	TP*
	1	0.33	0.07	4.7:1	44
	2	0.30	0.13	2.3:1	28
	3	0.27	0.18	1.5:1	20
	4	0.22	0.26	0.8:1	21
15	5	0.19	0.33	0.6:1	27
	6	0.15	0.40	0.4:1	32
	7	0.11	0.46	0.2:1	37
	8	0.07	0.53	0.1:1	58

20 \*TP for starting polymer before oxidation was about 45  
 cSt

Example 5

To 4000 grams of a chlorobenzene solution containing 8% by weight of the ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 were added 12.7 grams of cumene hydroperoxide and 29.7 grams of dicumyl peroxide with mixing. The reaction mixture was pumped at 33 g/min. into a 50 ml reactor tube (a one quarter inch (6.35 mm) stainless steel tubular reactor) which was maintained at 200°C and 200 psig (14.06 kg/cm<sup>2</sup>). The residence time in the reactor was 1.5 minutes.

To 500 grams of the reacted mixture were added 118.13 g of 100 Neutral oil. The chlorobenzene was removed from this mixture by distillation at 200°C and 20 mm Hg pressure.

A portion of the final product solution was then diluted to 2.8% by weight polymer using additional 100

- 1 Neutral oil. The viscosity (Thickening Power) of the resulting 2.8% solution at 100°C was 12.7 cSt. The oxygen content of the product as determined by Neutron Activation Analysis was 0.33%. The acid content was
- 5 2.8 mmole COOH/100 g polymer and the hydroxyl content was 0.069 mmoles OH/100 g polymer.

Multi-grade lubricating oils with good dispersancy and shear stability were prepared using the product of this Example.

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Example 6

Lubricating oil compositions in accordance with this invention was evaluated in the standard Sequence V-D automotive engine test. In the Sequence V-D test, lubricants containing the experimental additives are charged respectively to a standard internal combustion engine. The engine is operated at an assigned load and temperature, and at the end of a prescribed time the engines are disassembled and examined for deposits and wear. This engine test is a standard method well known in the industry.

Also, viscosity measurements at 100°C, 40°C and 0°C show acceptable viscosity measurements and with the use of pour point depressants, acceptable viscosity measurements at -32°C are obtained.

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A. Standard Sequence V-D Engine Test

Formulated 10W-30 oils (Exxon 150 neutral) containing the viscosity index improvement additives shown in Table I were prepared and tested in a Sequence V-D Test method phase 9-2 (according to candidate test for ASTM) as shown in Table II below. This procedure utilizes a Ford 2.3-litre four-cylinder engine. The test method simulates a type of severe field test service characterized by a combination of low speed, low temperature "stop and go" city driving and moderate motorway operation. The effectiveness of the additives in the oil is measured in terms of the protection provided against deposits and valve train wear. Each of

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1. the formulated 10W-30 oils also contained 3.5% of a polyisobutylene succinimide (50% by weight concentrate in oil), 20 mmoles/kg overbased calcium sulfonate, 30 mmoles overbased magnesium sulfonate, 18 mmoles dialkyl dithiophosphate, 0.3% dialkyl diphenylamine and 1% of a sulfonate-succinimide reaction product overbased with potassium triborate.

TABLE II  
Sequence V-D Performance

	Average <u>Formulation</u>	Piston <u>Sludge</u>	Average <u>Varnish</u>	Cam v. $10^{-3}$ Lab inch	Wear <u>Varnish</u> Avq. <u>Max.</u>
10	1.1% Product of Example 1	9.5	8.0	8.4	0.4 0.6
15	1.1% Product of Example 2	9.1	7.9	8.0	0.5 0.7
	1% Product of Example 3	8.6	7.8	7.7	0.5 0.8
	0.7% AMOCO 6565 <sup>1</sup>	9.4	8.1	7.3	0.6 0.7
20	0.7% TLA 555 <sup>2</sup>	9.1	7.7	8.0	0.5 0.7

<sup>1</sup>Commercial VI Improver - vinyl pyrrolidone grafted on to an ethylene/propylene copolymer.

<sup>2</sup>Commercial VI Improver - oxidized ethylene/propylene copolymer reacted with formaldehyde and an amine.

1   CLAIMS:

1.   A method of oxidatively degrading an olefinic polymer, which comprises oxidizing the olefinic polymer in an inert solvent in the absence of molecular oxygen  
5   and in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to  
10   1 to 0.4 to 1, whereby an oxidised polymer product is obtained.
2.   A method according to Claim 1, wherein the olefinic polymer is a copolymer of ethylene and a C<sub>3</sub>-C<sub>8</sub> alpha-olefin.
- 15   3.   A method according to Claim 2, wherein the olefinic polymer is an ethylene-propylene copolymer.
4.   A method according to Claim 1, wherein the olefinic polymer is a terpolymer of ethylene, a C<sub>3</sub>-C<sub>8</sub> alpha-olefin and a non-conjugated acyclic or alicyclic  
20   diolefin.
5.   A method according to Claim 4, wherein the olefinic polymer is a terpolymer of ethylene, propylene and 1,4-hexadiene.
- 25   6.   A method according to any preceding claim, wherein the oxidizing reaction is carried out at a temperature in the range from 60 to 250°C and under a pressure of from 0 to 1,000 psig (1 to 70.3 kg/cm<sup>2</sup>).
7.   A method according to any preceding claim,  
30   wherein the oxidant mixture is present in an amount of from 1 to 20% by weight, based on the olefinic polymer.
8.   A method according to any preceding claim,  
35   wherein the hydroperoxide in said oxidant mixture is hydrogen peroxide, cumene hydroperoxide, tertiary butyl hydroperoxide, or 2,5-dihydroperoxy-2,5-dimethylhexane, and the peroxide in said oxidant mixture is dicumyl peroxide, benzoyl peroxide, or dilauryl peroxide.

1 9. A method according to Claim 8, wherein the  
oxidant mixture comprises hydrogen peroxide and dicumyl  
peroxide.

10. A method according to Claim 8, wherein the  
5 oxidant mixture comprises cumene hydroperoxide and  
dicumyl peroxide.

11. A method according to any preceding claim and  
further comprising reacting the oxidised polymer product  
with an organic amine containing at least one primary or  
10 secondary amino group.

12. A method according to Claim 11, wherein the  
organic amine is a polyalkylene polyamine having the  
general formula:

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$$\text{H}_2\text{N}(\text{CH}_2\text{CHR}^1\text{NH})_x\text{H}$$
  
wherein each  $\text{R}^1$  is hydrogen or a  $\text{C}_1$  to  $\text{C}_6$  alkyl group and  
 $x$  is an integer in the range of from 1 to 10.

13. A method according to Claim 12, wherein the  
amine is ethylene diamine.

14. An oxidised polymer product obtained by the  
20 method claimed in any preceding claim.

15. A lubricating oil composition comprising an oil  
of lubricating viscosity and, as a viscosity index  
improvement agent, an oxidised polymer product as claimed  
in Claim 14.

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